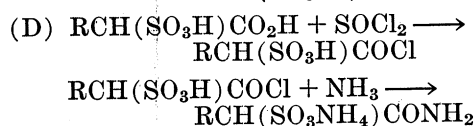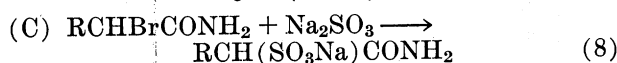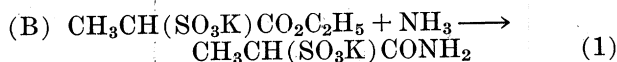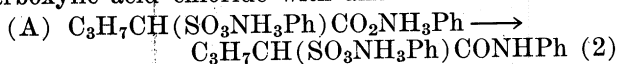# Amides of *a*-Sulfonated Palmitic and Stearic Acids

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AMIDES of a-sulfonated lower fatty acids have been prepared in the past by methods such as (A) the pyrolysis or dehydration of the amine salt; (B) the ammonolysis of the carboxylic acid ester; (C) the Strecker reaction of a-halogenated amides with a neutral sulfite; (D) the reaction of an a-sulfocarboxylic acid chloride with ammonia or an amine.

(A) $C_3H_7CH(SO_3NH_3Ph)CO_2NH_3Ph \longrightarrow$
$C_3H_7CH(SO_3NH_3Ph)CONHPh$ (2)

(B) $CH_3CH(SO_3K)CO_2C_2H_5 + NH_3 \longrightarrow$
$CH_3CH(SO_3K)CONH_2$ (1)

(C) $RCHBrCONH_2 + Na_2SO_3 \longrightarrow$
$RCH(SO_3Na)CONH_2$ (8)

(D) $RCH(SO_3H)CO_2H + SOCl_2 \longrightarrow$
$RCH(SO_3H)COCl$

$RCH(SO_3H)COCl + NH_3 \longrightarrow$
$RCH(SO_3NH_4)CONH_2$

In 1940 Mehta and Trivedi (8) applied the Hell-Volhard-Zelinskii and the Strecker reaction (C) to the preparation of long-chain a-sulfonated amides from the corresponding a-bromo-amides. The sodium salts of the a-sulfonated amides and N-methyl amides of lauric, myristic, palmitic, and stearic acid were prepared, and interfacial tension and wetting properties were measured.

The present report concerns the preparation of carboxylic acid chlorides of a-sulfonated palmitic and stearic acids (D), their conversion to simple and substituted amides, and the properties of the pure amides.

The action of chlorinating agents on sulfocarboxylic acids to produce acid chlorides has been variously reported. In 1875 Hemilian (7) found that phosphorus pentachloride reacts with a-sulfobutyric acid or the barium salt to produce a diacid chloride which decomposes to a-chlorobutyryl chloride and sulfur dioxide. This reaction has since been used to prove the structure of a-sulfonates (11) by comparison of the a-bromopalmitamide produced by the Hemilian method with that prepared by the Hell-Volhard-Zelinskii reaction. Others have found that diacid chlorides, such as $CH_2(SO_2Cl)COCl$ and $(CH_3)_2C(SO_2Cl)COCl$, are stable and may permit perferential esterification at the carboxylic acid chloride, followed by amide formation at the sulfonic acid chloride group (9, 10).

Chlorinating Agents

Since the acid chlorides of a-sulfopalmitic acid and a-sulfostearic acid were frequently dark viscous liquids, reagents for the preparation of acid chlorides were evaluated after conversion to the sodium or ammonium salt of the amide, which was easier to purify and analyze. Table I shows the results of experiments using phosphorus trichloride, phosphorus pentachloride, oxalyl chloride, and thionyl chloride to form acid hlorides from diacids, monosodium salts, and disodium salts of a-sulfonated palmitic or stearic acids,

TABLE I

Yield of Amide Using Different Chlorinating Agents, Percentage

	Form of a-Sulfonated Acid		
	Diacid	Monosodium salt	Disodium salt
PCl₃	3	....	None
PCl₅	24	....	45
(COCl)₂	2	None	35
SOCl₂	27	None	53
SOCl₂ (in excess)	47	5	58

by heating the reactants for about 1 hr. at 90°. The method for conversion to amides was the same in each case: a chloroform solution of the acid chloride was poured into a mixture of aqueous ammonia and ice. The presence of the sulfonic acid group seemed to facilitate hydrolysis. When ammonia gas was allowed to run into a solution of the acid chloride (a preferred method used in preparations described below) yields from the diacid and excess thionyl chloride were increased from 47% to 70%. Two moles of the chlorinating reagent were used except in the last experiment. Use of excess thionyl chloride, to act both as solvent and chlorinating agent, was the preferred method for the laboratory preparation of the amides.

The monosodium salts gave little or no reaction because of poor solubility in the chlorinating reagents. The disodium salts were not very soluble, but greater alkalinity caused the reaction to proceed with the removal of sodium chloride. Use of the diacid was generally preferred because of greater solubility and because any unconverted diacid was easily removed as the ammonium salt.

Preparation of *a*-Sulfonated Amides

The most satisfactory method for the preparation of carboxylic amides was found to be the reaction of the diacid with a large excess of purified thionyl chloride, followed by reaction of a cold chloroform solution of the acid chloride with the desired amine in an appropriate solvent. To illustrate details, the preparation of sodium N-hydroxyethyl-a-sulfostearamide is described.

a-Sulfostearic acid (12), 49.5 g. (0.136 mole), and 100 ml. (1.36 moles) of thionyl chloride, reagent grade redistilled over beeswax, were warmed together slowly at first to avoid foaming and then refluxed for an hour on the steam bath. Excess thionyl chloride was distilled off by using a water aspirator and heating on a boiling water bath. The dark viscous liquid residue was dissolved in 100 ml. of chloroform and cooled. The chloroform solution of the acid chloride was added dropwise to a stirred solution of 25 g. (0.44 mole) of ethanolamine in 100 ml. of chloroform, maintaining the temperature below 10° in an ice bath. After stirring for an additional hour, 95% ethanol was added, and chloroform was boiled off on the steam bath. The ethanolammonium salt of the hydroxyethyl amide was crystallized from the alcoholic solution at −20°. The product was taken up in 95% ethanol and made alkaline with 18 N NaOH; the sodium salt was crystallized from this solution at 0°. Another crystal-

TABLE II
Melting Point and Analyses of Salts of α-Sulfonated Amides

| RCH⟨CONHR'R''; SO₃M⟩		Glassy point °C.	Melting point °C.	% Na		% N		% S	
				Theo.	Found	Theo.	Found	Theo.	Found
α-Sulfopalmitamides									
Salt	Amide								
NH₄	—NH₂	170–1.5	180ᵃ	......	......ᵇ	7.95	7.67	9.10	8.89
Na	—NH₂	......	......	6.43	6.02	3.92	3.84	8.97	8.82
HOC₂H₄NH₃	—NHC₂H₄OH	102–4	......	......	......ᶜ	6.36	6.28	7.28	7.05
Na	—NHC₂H₄OH	......	......	5.72	5.64	3.49	3.43	7.99	8.07
Na	—NHC₂H₅	105	188.5–189	5.96	5.79	3.63	3.46	8.32	8.20
α-Sulfostearamides									
Salt	Amide								
NH₄	—NH₂	172–4	183ᵃ	......	......ᵈ	7.36	7.19	8.43	8.55
Na	—NH₂	......	......	5.96	5.86	3.63	3.69	8.32	8.15
HOC₂H₄NH₃	—NHC₂H₄OH	103–5	......	......	......ᵉ	5.98	6.03	6.84	7.02
Na	—NHC₂H₄OH	......	......	5.35	5.22	3.26	3.32	7.47	7.39
Na	—NHC₂H₅	143–54	184–5	5.56	5.49	3.39	3.23	7.75	7.59
Na	—NHCH₂CHOHCH₃	78–9	164–5	5.18	5.08	3.16	3.05	7.23	7.06
Na	—N(C₂H₄OH)₂	85	198ᵃ	4.86	4.73	2.96	2.32	6.77	7.18
Na	—N(C₂H₄SO₃Na)(CH₃)	......	......	8.69	8.03	2.64	2.54	12.10	11.66

ᵃ Melting with decomposition.
ᵇ, ᶜ, ᵈ, ᵉ Neutral equivalents 362, 440, 386, 472, respectively.

lization from 95% ethanol gave a white product in 24% yield, with the analysis shown in Table II.

Simple amides were made by passing dry NH_3 gas into a chloroform solution of the acid chloride. Ethyl amides were prepared by pouring a cold chloroform solution of the acid chloride into a mixture of ice and 33% aqueous ethylamine. The sodium salt of N-methyltaurine, obtained by evaporation of a commercial 35% aqueous solution, was suspended in a carbon tetrachloride solution of the acid chloride, and the mixture was heated at reflux temperature to form the amide.

The ethyl amides and the isopropyl alcohol amide were the only compounds with sharp melting-points. Eight compounds gave a sharp change to a glassy appearance at temperatures recorded in Table II. Seven compounds did not melt nor decompose below 200°.

Infrared Examination. Amide and Diamide Formation. Infrared examination by the mull technique of a typical preparation from the acid chloride and ethanolamine confirmed amide

$$RCH(SO_3Na)CONHC_2H_4OH$$
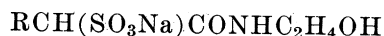
rather than ester-amine

$$RCH(SO_3Na)CO_2C_2H_4NH_2$$
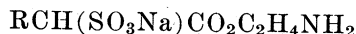
formation. A sharp band characteristic of amides was found at 1550 cm.⁻¹ and a broad band at 3400–3500 cm.⁻¹ indicative of the hydroxyl group. Absence of broad absorption at 1580–1650 cm.⁻¹ showed the absence of primary amine, and there was no absorption in the ester region above 1700 cm.⁻¹.

In the purification of amides it was sometimes necessary to extract an alcoholic solution of the amide with toluene to remove a small amount of neutral by-product assumed to be the corresponding diamide. Isolation of the by-product from the preparation of sodium α-sulfostearamide gave a white solid with the following analysis: calculated for $C_{18}H_{38}N_2O_3S$, 59.63% C, 10.56% H. 7.73% N, 8.84% S; found, 59.43% C, 11.00% H, 7.32% N, 8.46% S, 1.27% Cl, 0.51% Na.

Infrared examination, using the KBr disk method, revealed both adsorption at 1680 cm.⁻¹ and 1616 cm.⁻¹ characteristic of carboxylic amides, and adsorption at 1152 cm.⁻¹ and 1319 cm.⁻¹ characteristic of sulfon-

amides. Reduction of adsorption in the sulfonate regions (1047 cm.⁻¹ and 1214 cm.⁻¹) as compared with a sample of sodium α-sulfostearamide suggests the presence of 10% monoamide. From the infrared data and the elemental analysis the material is principally the diamide of α-sulfostearic acid. The impurities are the sulfonated mono-amide, solubilized inorganic chloride, and possibly a small amount of the α-chlorostearamide.

Solubility and Surface-Active Properties

Krafft Point. Solubility of the α-sulfonated amides was compared by the Krafft point technique (5) for 1% solutions, as shown in Table III. Lower Krafft

Amine, NHR'R''	Cation, M+	Sulfopalmitic R = C₁₄H₂₉	Sulfostearic R = C₁₆H₃₃
NH₃	NH₄	85	>100
NH₃	Na	61	78
NH₂C₂H₄OH	HOC₂H₄NH₃	5	25
NH₂C₂H₄OH	Na	34	42
NH₂CH₂CHOHCH₃	Na	....	5
NH₂C₂H₅	Na	29	38
NH(C₂H₄OH)₂	Na	....	5
NH(CH₃)C₂H₄SO₃Na	Na	....	5

points or greater solubility were found for compounds with greater substitution at the nitrogen atom. Hydroxyethyl amides were slightly less soluble than corresponding ethyl amides. Ethanolammonium salts of hydroxyethyl amides were more soluble than the sodium salts, but unsubstituted ammonium salts of amides were less soluble than corresponding sodium salts. All of the compounds with Krafft points below room temperature were capable of forming clear 10% aqueous solutions at room temperature.

All of these compounds may be dissolved in aqueous alcohol, and the more highly substituted amides are soluble in absolute ethanol at room temperature. It is possible to form a 1% solution of sodium di-(N-hydroxyethyl)-α-sulfostearamide in chloroform at room temperature.

c.m.c. Critical micelle concentrations measured by the dye titration method (4) at room temperature were as follows, in millimoles per liter:

sodium N-hydroxyethyl-α-sulfopalmitamide	0.62
sodium N-ethyl-α-sulfopalmitamide	0.61
ethanolammonium N-hydroxyethyl-α-sulfopalmitamide	0.37
sodium N-ethyl-α-sulfostearamide	0.18
sodium N-(2-hydroxypropyl)-α-sulfostearamide	0.11

These values show an expected decrease with increase in length of the carbon chain and little difference between ethyl amide and hydroxyethyl amide. For comparison the values reported (13) for the esters, sodium ethyl α-sulfopalmitate and sodium ethyl α-sulfostearate, were 0.34 and 0.05, respectively.

Stability to Calcium and Other Ions. Calcium stability values are shown in Table IV. Sodium salts of

TABLE IV
Surface-Active Properties of Sodium Salts of α-Sulfonated Amides

CONR′R″ / RCH< / SO₃Na	Surface tension 0.1% solution 25° dynes/cm.	Lime soap-dispersion value (3)	Calcium stability (14) 25° p.p.m. CaCO₃
α-Sulfopalmitamides			
—NH₂	....	5	430$^{(50°)}$
—NHC₂H₄OH	43	7	>1800
—NHC₂H₅	40	6	840
α-Sulfostearamides			
—NHC₂H₄OH	42	5	1540
—NHCH₂CHOHCH₃	40	7	1350
—N(C₂H₄OH)₂	50	18	1500
—N(CH₃)C₂H₄SO₃Na	37	7	>1800

α-sulfonated amids soluble to the extent of 0.5%, as required by the test conditions, had excellent calcium stability.

The stability of the sodium salts of Table IV (with the exception of sodium α-sulfopalmitamide) to other metallic ions was measured by the method of Harris (6). All had excellent metallic ion stability with values of 100, to Mg^{++}, Fe^{++}, Ni^{++}, Cu^{++} and Zn^{++}, except the value for sodium N-hydroxyethyl-α-sulfostearamide was 44.0 with respect to Fe^{++}. Metallic ion stability values with respect to Ba^{++} ranged from 13.3 to 35.0, Pb^{++} 32.0 to 83.4, Al^{+++} 9.0 to 100. Disodium N-methyl, N-(2-sulfoethyl)-α-sulfostearamide had the best metallic ion stability with a value of 100 for six ions, 35.0 for Ba^{++} and 83.4 for Pb^{++}.

Surface and Interfacial Tension. Surface-tension measurements, using the duNoüy method, are recorded in Table IV. Interfacial tension values against light petrolatum ranged from 7 for disodium N-methyl, N-(2-sulfoethyl)-α-sulfostearamide to 18 for sodium di-(N-hydroxyethyl)-α-sulfostearamide, in the same order as that shown for surface-tension values.

Lime Soap-Dispersing Power. All of the α-sulfonated amides were found to have good lime soap-dispersing values. Increased substitution at the nitrogen atom, in the case of the diethanolamide, caused some loss in lime soap-dispersing power. The values of Table IV compare favorably with values of 35% for sodium dodecyl sulfate and 8% for a commercial sodium N-methyl,N-oleoyltaurate. The ability to disperse lime soap curd indicates the α-sulfonated amides may find use in soap-syndet combinations.

Summary

Carboxylic acid amides of α-sulfopalmitic and α-sulfostearic acids were prepared from ammonia, ethylamine, ethanolamine, isopropylalcoholamine, diethanolamine, and N-methyltaurine, and were isolated as the sodium, ammonium, or ethanolammonium salt.

A satisfactory method was found to be the reaction of the sulfocarboxylic acid with an excess of thionyl chloride, and further reaction of the acid chloride with an amine in a chlorinated solvent. More work is needed on the application of direct amidation methods to the preparation of these compounds.

The solubility of the α-sulfonated amides increased with substitution of alkyl, hydroxyalkyl, and sulfoalkyl groups at the nitrogen atom. Ethanolammonium N-hydroxyethyl-α-sulfopalmitamide, ethanolammonium N-hydroxyethyl-α-sulfostearamide, sodium N-(2-hydroxypropyl)-α-sulfostearamide, sodium di-(N-hydroxyethyl)-α-sulfostearamide, and disodium N-methyl,N-(2-sulfoethyl)-α-sulfostearamide have aqueous solubility in excess of 10% at room temperature.

Most of the sodium salts of the α-sulfonated amides have good or excellent stability to calcium and other divalent ions and are excellent lime soap dispersing agents.

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